

PATENT SPECIFICATION

1,063,268

DRAWINGS ATTACHED.

1,063,268



Date of Application and filing Complete Specification:
Oct. 9, 1963. No. 39861/63.

Application made in Italy (No. 20027) on Oct. 11, 1962.

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COMPLETE SPECIFICATION.

Method for Preparing Ketones Containing a Cyclohexylic Nucleus.

ERRATA

SPECIFICATION NO. 1,063,268

Page 3, line 43, for "8,937" read "8.937"

Page 3, line 114, for "3,884" read "3.884"

Page 3, line 115, for "0.01" read "1.01"

Page 3, line 120, for "cyclohexyketone" read "cyclohexylketone"

Page 4, line 55, for "enting" read "entering"

Page 4, line 92, for "that" (first occurrence) read "what"

Page 4, line 123, for "of" read "off"

Page 5, line 26, for "predetermined" read "predetermined"

Page 5, line 48, for "stirring" read "stirring"

THE PATENT OFFICE,
25th April, 1967

D 83908/16

30 The methods proposed hitherto show furthermore the drawback that the molten mass of the catalyst decreases during the operation and that, although the yield is not varied by this fact, the ketones formed assume gradually a more and more intense colour.

35 It has been found, and this forms the object of the present invention, that a simple modification in the above referred to methods, leads not only to practically quan-

stop cocks. While the acids are introduced, the stop cock controlling the downward condenser is closed, and the cock controlling the reflux condenser is opened. The water formed during the introduction of the acids is collected in a container put under the end of the condenser. After addition of a predetermined amount of acid, the cock controlling the reflux condenser is closed and that of the downward condenser is opened.

80 Instead of a downward condenser, it is advantageous to use an apparatus assembly of the type illustrated in Fig. 1 of the accompanying drawings, at the right-hand side of the round bottomed flask.

[Price 4s. 6d.]

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COMPLETE SPECIFICATION.

Method for Preparing Ketones Containing a Cyclohexylic Nucleus.

We, SNIA VISCOSA SOCIETA' NAZIONALE INDUSTRIA APPLICAZIONI VISCOSA S.p.a., of Via Cernaia 8, Milan, Italy, an Italian Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The British Patent Applications No. 22011/63 (Serial No. 1,030,003) and No. 29161/63 (Serial No. 1,063,268) filed by applicants have disclosed methods for producing cyclohexylphenyl-ketone and dicyclohexylketone with practically quantitative yields, as calculated with reference to the reacting acids, with the use of metal oxides as catalysts, in particular manganese oxide dissolved in the corresponding acids. The methods described in said prior applications show, however, the drawback consisting in that although leading to substantially quantitative yields, the conversion of the acids subjected to the ketonization reaches only 70 to 90%.

In order to obtain by the hitherto known methods the highest possible conversion rate cylindrically shaped reactors were used. The molten mass is made to circulate in the reactors and the acids are introduced either in the vapor state in countercurrent or liquified or vaporized coming from the bottom of the reactor.

The methods proposed hitherto show furthermore the drawback that the molten mass of the catalyst decreases during the operation and that, although the yield is not varied by this fact, the ketones formed assume gradually a more and more intense colour.

It has been found, and this forms the object of the present invention, that a simple modification in the above referred to methods, leads not only to practically quan-

titative yields of cyclohexylphenylketone and dicyclohexylketone, but also to practically quantitative conversions of the acids into ketones which moreover are obtained entirely free of carbohexylic acids or containing only very small amounts of them.

This simple modification allows furthermore to maintain unvaried the amount of the catalyst for a long production period whereby its activity is prolonged.

The novel methods differ from those proposed hitherto by the fact that the adsorption of the acids at the metal oxides (salt formation) is carried out independently of the preparation of the ketone.

In the most simple case, one operates with a single reactor and in such a manner as to prevent the ketones and the acids from distilling during the first stage of the process—that is during the introduction of the acids to be ketonized into the catalyst—and to interrupt on the other hand the introduction of the acids during the second stage of the process, that is during the distillation of the ketones. It is possible to separate the two operation stages for instance by applying a reflux condenser and a downward condenser, both of which are provided with suitable stop cocks. While the acids are introduced, the stop cock controlling the downward condenser is closed, and the cock controlling the reflux condenser is opened. The water formed during the introduction of the acids is collected in a container put under the end of the condenser. After addition of a predetermined amount of acid, the cock controlling the reflux condenser is closed and that of the downward condenser is opened.

Instead of a downward condenser, it is advantageous to use an apparatus assembly of the type illustrated in Fig. 1 of the accompanying drawings, at the right-hand side of the round bottomed flask.

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In order to maintain constant the volume of the catalyst it is necessary to introduce into the flask from time to time a volume of acid corresponding substantially to the volume of the distilled ketone, taking into account that due to the loss of CO_2 and water the amount of ketone distilled off is smaller than the amount of acid introduced. The specific gravities of the acids and of the ketone are almost equal, and from 128 gr. of hexahydrobenzoic acid and 122 gr. of benzoic acid, (equal to an acid mixture of 250 gr.) there are obtained 188 gr. of cyclohexylphenylketone, and from 256 gr. of hexahydrobenzoic acid, there are obtained 194 gr. of dicyclohexylketone what means that there are obtained about 0.75 cc. of ketone for each cc. of acid introduced into the reaction. The ketonization and the absorption of the acids may be also carried out separately in two different reaction vessels in which the catalyst circulates permanently by means of a heated pump. It is of advantage to maintain in the reaction vessel in which the absorption takes place a slightly lower temperature than in the reaction vessel in which the ketonization is effected.

In order to prepare the mixed ketone (cyclohexylphenylketone), it is of advantage to operate with practically equimolecular amounts of benzoic acid and hexahydrobenzoic acid. Moreover, it is also possible to operate with a slight molar excess, (0.1 to 2% and at most 5%) of hexahydrobenzoic acid related to the benzoic acid. Such an excess is found again in the end product either as dicyclohexylketone, or as unchanged hexylhydrobenzoic acid.

The novel method differs from those described in the above-referred patent applications solely by the fact that the absorption of the metal oxides by the acids with a view to preparing the metal salts thereof, is executed separately of the ketonizing reaction. Furthermore, when operating in accordance with the improved method, it is possible also to resort only to a manganese salt, or else, to a manganese salt in mixture with other metal salts, or else, it is possible to work entirely with the latter.

It is also advantageous to blow steam into the reaction mass as well during the absorption stage as during the ketonization reaction, or else, only during one of the two stages. Also the introducing of hydrogen into the reacting mass results in an advantageous protection of the catalyst, if required, against any possible oxidation.

The improved method will be better disclosed with further details with reference to the following non-limiting examples illustrated by the accompanying drawings. In said drawings, Figs. 1 and 2, two different apparatus for executing the method are shown.

In the apparatus of Fig. 1, the coil 1 serves for super-heating steam, while 2 designates a funnel containing the acid and 3 designates the reaction flask. 4 is a stirrer provided with angularly adjustable blades, 5 is thermometer, 6 a water cooled bulbs-condenser, 7 a water collecting trap, 8 a drain-cock for the water, 9 a drain cock for the condensed product, 10 a collecting receiver for the condensed product, 11, 12 a so-called Dreehsel bubbling scrubber for CO_2 , and 13 a gas meter.

In Fig. 2, A designates a salt-producing reaction vessel, B a ketonizing reactor, 1 a pump for introducing acids, while 2—3 and 11—12 designate stirrers, 4 & 13 tubes for thermometers, 5 & 14 filling tubes, 6 a steam super-heating coil, 7 a siphon, 8 a water trap, 9, 10 condensers, 15 a circulating pump for the catalytic mass, 16 a distilling tube, 17 a siphon for continuous draining, 18 a receiver, 19 tubes for removing the gas and 20 a gasmeter.

EXAMPLE I:

a) Preparation of the catalyst:

Into a flask of a capacity of 2 litres and provided with a reflux condenser, a stirrer, a thermometer, a tube for gas inlet, and a dropping funnel, there are introduced 524 gr. of commercial manganese carbonate (containing 42% of metallic manganese corresponding to four moles) and 488 gr. of hexahydrobenzoic acid. The mixture is heated under stirring to $110\text{--}120^\circ\text{C}$ and maintained at this temperature for one hour blowing in simultaneously a steam of hydrogen. There are then added 488 gr. more of hexahydrobenzoic acid, the molar ratio between manganese and hexahydrobenzoic acid becoming thus equal to 1:1.9. The reflux condenser is replaced by a downward condenser and the mixture is heated slowly during two hours up to 370°C while the water is distilled off which carries away 39 gr. of acid and CO_2 , is evolved. There remain in the flask 1,210 gr. of catalyst.

b) Preparation of the ketone:

The flask is now connected with the apparatus illustrated in Fig. 1 the cock 9 is opened and introducing super-heated steam the reaction mass is heated under stirring at $390\text{--}395^\circ\text{C}$ until in the container 10 there are collected 150 cub.cm. of organic liquid. Now the cock 9 is closed and within twelve minutes, 200 gr. of hexahydrobenzoic acid are allowed to flow from the container 2 into the flask. The acid is speedily absorbed by the catalytic mass. The water coming by the superheating coil 1 and the water formed during the reaction is collected in the water trap 7 and is drawn off from time to time. Now the temperature of the reaction mass which in the meantime

has fallen to 380–385°C is raised again to 390°C within three to five minutes. During this time the valve 9 is opened and, within twelve to fifteen minutes, there distills a further volume of 150 cub.cm. of organic material, while the temperature of the reacting mass rises again to 398°C. The procedure is repeated at uniform intervals and is cut off after twenty hours.

From the total 8000 gr. of hexahydrobenzoic acid introduced into the apparatus during said twenty hours, there are obtained 6027 gr. of organic substance, of which 5950 are formed by dicyclohexylketone, 48 gr. by unchanged hexahydrobenzoic acid and 17 gr. by a substance having a high boiling point. In the flask there remain still 1.175 gr. of a catalyst of which a sample is taken for determining its components. The analysis is carried out as follows: the sample is heated at first with an excess of hydrochloric acid until the manganese has been dissolved in the water as chloride. The organic layer is separated and distilled. There remain a few grs. of a product having a high boiling point.

The distillate is shaken with a sodium carbonate solution of 10% and the alkaline aqueous layer is separated and acidified. The hexahydrobenzoic acid precipitates as an oily layer. The organic layer of the distillate is pure dicyclohexylketone (identified by its refraction index which is $n_D^{14} = 1.484$ (Beilstein VII, 143).

Applying the results obtained from the sample to the total mass of the catalyst, it appears that besides the manganese, the catalyst contains still 95 gr. of dicyclohexylketone, 790 gr. of hexahydrobenzoic acid and 21 gr. of a product having a high boiling point.

Taking into account the total amount of 8,937 gr. of acid introduced into the process and the total amount of 838 gr. of acid recovered, there is obtained a total yield of 6045 gr. of dicyclohexylketone corresponding to 98.4% of the theoretical amount. The conversion calculated with reference to the ratio between the hexahydrobenzoic acid transformed into ketone and the non-transformed hexahydrobenzoic acid contained in the distillate, results in being 98.3% of the theoretical amount.

EXAMPLE II:

The same apparatus described in Example I (as illustrated in Fig. 1) is used for the preparation both of the catalyst and of the ketone.

a) Preparation of the catalyst:

Into the flask, there are introduced 524 gr. of commercial manganese carbonate (containing 42% of metallic manganese cor-

responding to four moles), 251 gr. of hexahydrobenzoic acid corresponding to 1.96 moles and 237 gr. of benzoic acid corresponding to 1.94 moles. Under stirring and under blowing in hydrogen the mixture is maintained at a temperature of 110 to 120°C. during one hour. Then, there are added further 251 gr. of hexahydrobenzoic acid and 237 gr. of benzoic acid (the molar ratio between the manganese and the total amount of acids becoming thus 1:1.975). The reflux condenser is replaced by a downward condenser and the mixture is heated under stirring during a period of two hours at a temperature of 330°C. The water is distilled off and CO₂ is evolved. The mass of catalyst remaining in the flask weighs 1256 gr.

b) Preparation of the cyclohexylphenylketone:

The flask is connected to the apparatus illustrated in Fig. 1; the cock 9 is opened and the mass contained in the flask is heated, under stirring and introducing super-heated steam at a temperature of 335–340°C, until in the trap 7 there are collected 150 cc. of the organic liquid. The cock 9 is then closed and within twelve minutes 200 gr. of a mixture of hexahydrobenzoic acid and benzoic acid are allowed to flow from the funnel 2 into the flask 3 (there are used 102.9 gr. of hexahydrobenzoic acid and 97.1 gr. of benzoic acid with a molar ratio equal to 1.01:1).

The absorption takes place immediately and water is formed which, together with the water coming from the superheating coil 1, is collected in the trap 7 and is drawn off from time to time. The temperature of the reacting mass which in the meantime has fallen to 328–330°C raised again to 340°C in about 3 minutes. In the meantime, the cock 9 is opened.

Within 15 minutes further 150 cc. of organic material are distilled while the temperature of the reacting mass rises again to 342°C.

The procedure is repeated at uniform intervals and is cut off after twenty hours.

From the total 8,000 gr. of acid mixture (4,116 gr. of hexahydrobenzoic acid and 3,884 gr. of benzoic acid: molar ratio equal to 0.01:1) introduced into the apparatus during said twenty hours, there are obtained 6,050 gr. of an organic distillate which, when treated in the manner described in Example I, give 5,955 gr. of cyclohexylphenylketone, 40 gr. of cyclohexylketone, 32 gr. of hexahydrobenzoic acid and 5 gr. of products having a high boiling point.

In the flask, there remain 1.164 gr. of the catalyst which, treated as described in Example I, give still 372 gr. of hexahydrobenzoic acid, 373 gr. of benzoic acid, 110 gr.

of cyclohexylphenylketones and 17 gr. of products having a high boiling point (the ratio between the hexahydrobenzoic acid and the benzoic acid is defined by resorting to the refraction index of the distillate: see Fig. 4).

The yield and conversion rate are calculated as described in Example I, without taking into account the small excess of 0.01 moles of hexahydrobenzoic acid with reference for 1 mole of benzoic acid, found either in the distillate or in the catalytic mass under the form of dicyclohexylketone. The yield of cyclohexylphenylketone is equal to 99% of the theoretical amount. Also the conversion is equal to 99% of the theoretical amount.

EXAMPLE III:

Both for the preparation of the catalyst and for the ketonization of the acid mixture, there is used an apparatus made of stainless steel (see Fig. 2).

a) Preparation of the catalyst:

In the reactor A there are put 5,240 Kg. (=40 moles) of commercial manganese carbonate (containing 42% of metallic manganese) 2,500 kg. of hexahydrobenzoic acid (or 19.55 moles) and 2,379 kg. of benzoic acid (or 19.5 moles). The mixture is heated under stirring (40 r.p.m.) in a light current of hydrogen maintaining its temperature at 110/120°C during one hour. Then there are introduced further 2,502 kg. of hexahydrobenzoic acid and 2,379 kg. of benzoic acid (the molar ratio between manganese and the acid mixture becomes 1:1.95) and the mass is slowly heated during two hours to a temperature of 320°C. The water formed (1,310 kg.) is collected in the collecting vessel 8, while the CO₂ produced by the manganese carbonate passes the gas-meter 20. The catalytic mass remaining in the reaction vessel A weighs 11,915 kg, and its specific gravity is equal to 1.3.

The same reaction is repeated with the same amounts in the reactor vessel B. The water formed is removed through the siphon 17.

b) Continuous preparation of cyclohexylphenylketone:

The catalytic masses obtained in the reaction vessels A and B are then heated to 320/325°C under stirring (40 r.p.m.) while a weak stream of superheated steam is blown into said masses, entering through the coil 6 and the feeding pipe 21. The use of steam in the reactor A is substantially of no influence. The temperature of the catalyst mass contained in the reactor B is raised to the temperature of 342/343°C. required for ketonization. Within ten minutes there distill through the pipe 16, 750 cc. of organic

material which passing through the siphon 17 reach finally the collecting receiver 18.

Now, by means of the gear pump 15, having a capacity of 8 kg. per hour and being heated to 320/325°C, the mass of the reactor vessel B returns into the reaction vessel A. Simultaneously and within one hour, by the gear pump 1 kept at a temperature of 110°C, there are fed further 6 kg. of the acid mixture heated to 100/110°C into the reactor A. The 6 kg. of the acid mixture are composed of 3,083 kg. of hexahydrobenzoic acid and of 2,917 kg. of benzoic acid, (the molar ratio being as 1.01:1).

The acid mixture is immediately absorbed by the catalytic mass in the reactor A.

In order to check the progression of the reaction inside the reactor A, one resorts to a scaled rod which is introduced into the mass through the filling tube 5 at intervals of about thirty minutes.

It is thus possible to check the level of the liquid inside the reaction vessel A and it is also possible to check whether the mass still contains some undissolved manganese oxide (the sample removed with the rod should show the green color of manganese oxide). If all the manganese oxide should be dissolved, that would indicate that an excess of acids is present, the delivery of the pump 15 ought to be increased.

The temperature of the reactor A is maintained at a constant value of 300/310°C. The water produced during the formation of the salts and also by the condensation of the steam introduced, is condensed in the condenser 9. The water is collected in the collecting trap 8 and is discharged from time to time.

The temperature of the reactor B inside of which the ketonization takes place is maintained at a constant value of 342/343°C, while the reaction vessel B is fed continuously through the siphon 7 with the mass of absorbed acids present inside the reactor A.

The reaction is carried out in such a manner, that within ten minutes, 1,000 cc. of the mixture of acids are recycled in the reaction vessel A, and that 750 cc. of organic substance are distilled off from the reactor B.

The regular progress of the reaction is checked continuously by various measurements and, in particular as follows:

- by the measurement of amount of CO₂ (measuring instrument 20) evolved during a predetermined time.
- by the amount of organic substance distilled off within the same time.

For instance there is collected an organic product distilled within 10 minutes exactly, the volume of which should be equal to 750 cc. If within said ten minutes there distills

from the reactor B a volume less than 750 cc. of the organic product and if the same time less than 100 litres of gas are evolved, the temperature of the reactor B is to be increased by 2 to 3°C, until the amount of the organic product distilled and of gas evolved has reached again its normal value.

On the other hand, when within said ten minutes, there are evolved more than 100 litres of gas and there distill more than 750 cc. of organic substance the temperature in the reactor B is lowered by 2 to 3°C until the amount of gas and the amount of organic substance have returned to their normal values.

At a temperature inside the reactor B, held constantly at 342—343°C, the amounts indicated for the gas and the distillate reach the minimum predetermined value. Therefore, during the 60 hour's test described, it was for instance necessary to increase repeatedly the temperature by about 2°C.

Furthermore, as third checking means serves the temperature inside the reactor B giving an index for the progression of the distillation. If, during a predetermined period of time, a too great amount is distilled, the temperature rises up to 350°C, while it falls down to 338/340°C if the amount of the distillate diminishes too much.

The amount of the distilled product passed through the siphon 17 is continuously collected in the receiver 18 and reaches a value of 4.6 to 4.8 litres per hour, the water being included in said figure.

After sixty hours, the reaction is stopped. During said time, 360.5 kg. of a mixture of acids (184.98 kg. of hexahydrobenzoic acid and 175.52 kg. of benzoic acid) have reacted and there have been obtained 269.36 kg. of organic distillate which, when distilled again, gives 268.6 kg. of a distillable product and 0.7 kg. of a residue having a high boiling point.

A sample is taken off and its contents of unchanged hexahydrobenzoic acid is terminated, by stirring it with a solution of sodium carbonate of 10%, separating the alkaline aqueous layer, acidifying it and titrating the hexahydrobenzoic acid. The amount of the latter contained in the total of the distillate is 1.1 kg.

The remainder of the distillate weighing 267.5 kg. consists of cyclohexylphenylketone (identified on a sample, as being free from any hexahydrobenzoic acid as shown by its refraction index which is equal to the n_D^{20} 1.5236 (7)—See Figure 3). The catalytic mass

treated as described in Example I contains still 7.4 kg. of hexahydrobenzoic acid, 7.27 kg. of benzoic acid (determined by the refraction index of the mixture), 1.87 kg. of cyclohexylphenylketone and 0.27 kg. of products having a high boiling point.

Taking into account the total amount of the acid mixture equal to 380 kg. (195 kg. of hexahydrobenzoic acid and 185 kg. of benzoic acid), and the total amount of 8.5 kg. of hexahydrobenzoic acid and 7.3 kg. of benzoic acid which has been recovered, the total yield of cyclohexylphenylketone obtained is 269.4 kg. which corresponds to 98.4% of the theoretical amount.

The conversion calculated as in the case in Example I is equal to 99.9%.

WHAT WE CLAIM IS:—

1. A method for preparing dicyclohexylketone and cyclohexylphenylketone by the conversion of hexahydrobenzoic acid or of an equimolecular mixture of hexahydrobenzoic acid with benzoic acid at temperatures ranging between 280 and 450°C in the presence of metal oxides, in particular manganese oxide, dissolved in the corresponding acids, said method consisting in that to increase the activity of the catalyst and to increase the conversion ratio the reaction of the acids with the metal oxide on the one hand and the conversion of said acids into ketones on the other hand are executed in two successive stages.

2. A method as claimed in claim 1, according to which the reaction of the acids with the metal oxide and their conversion, are executed in the same reaction vessel but in two successive stages, thus preventing the distillation of the ketones during the introduction of the acids and stopping the introduction of the acids during the distillation of the ketones.

3. A method as claimed in claim 1, according to which the reaction between the acids and the metal oxides on the one hand and the conversion into ketone on the other hand, are executed in separate reactors.

4. A method for preparing dicyclohexylketone and cyclohexylphenylketone as claimed in claim 1, substantially as described.

SNIA VISCOSA SOCIETA' NAZIONALE
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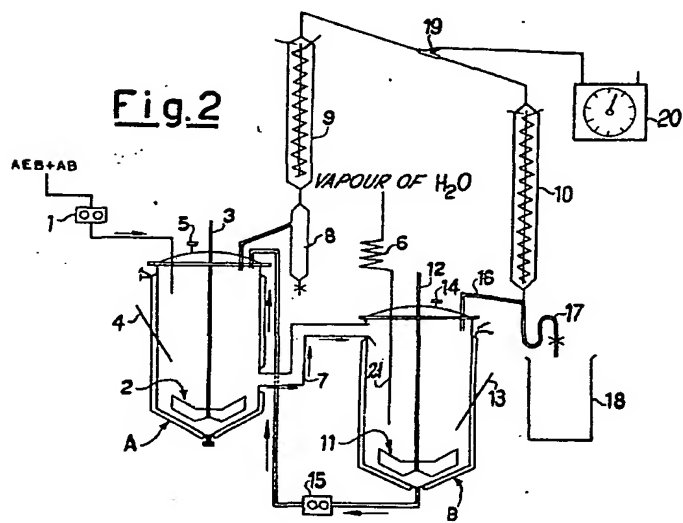
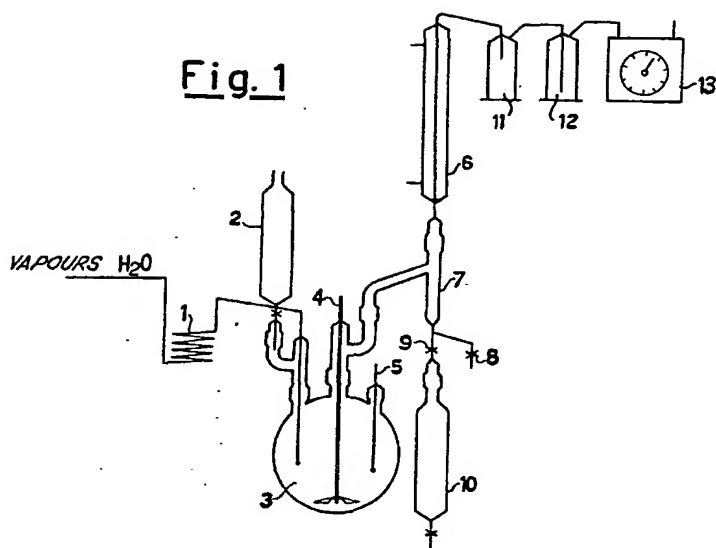


Fig. 3.

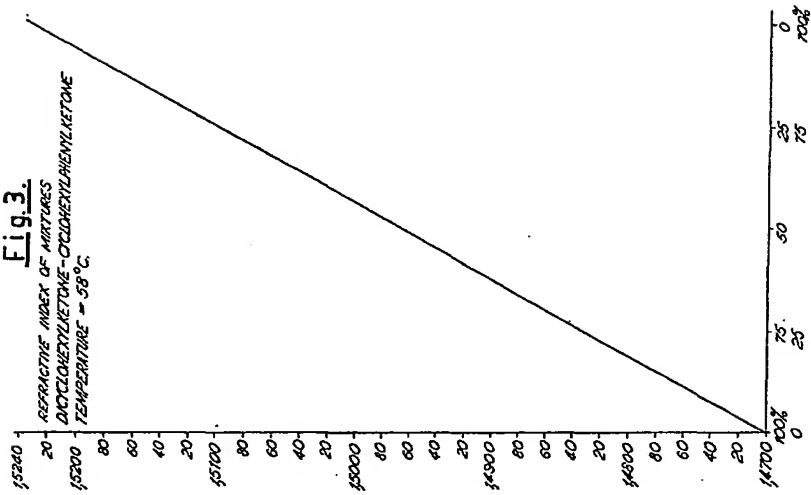


Fig. 4.

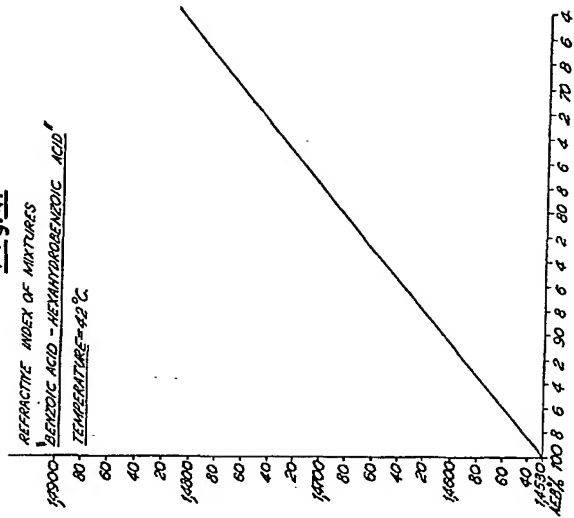
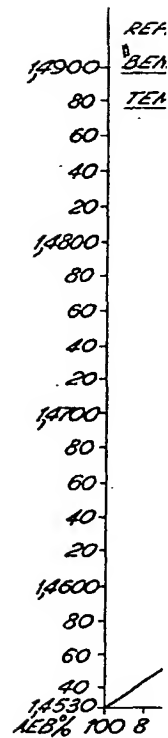
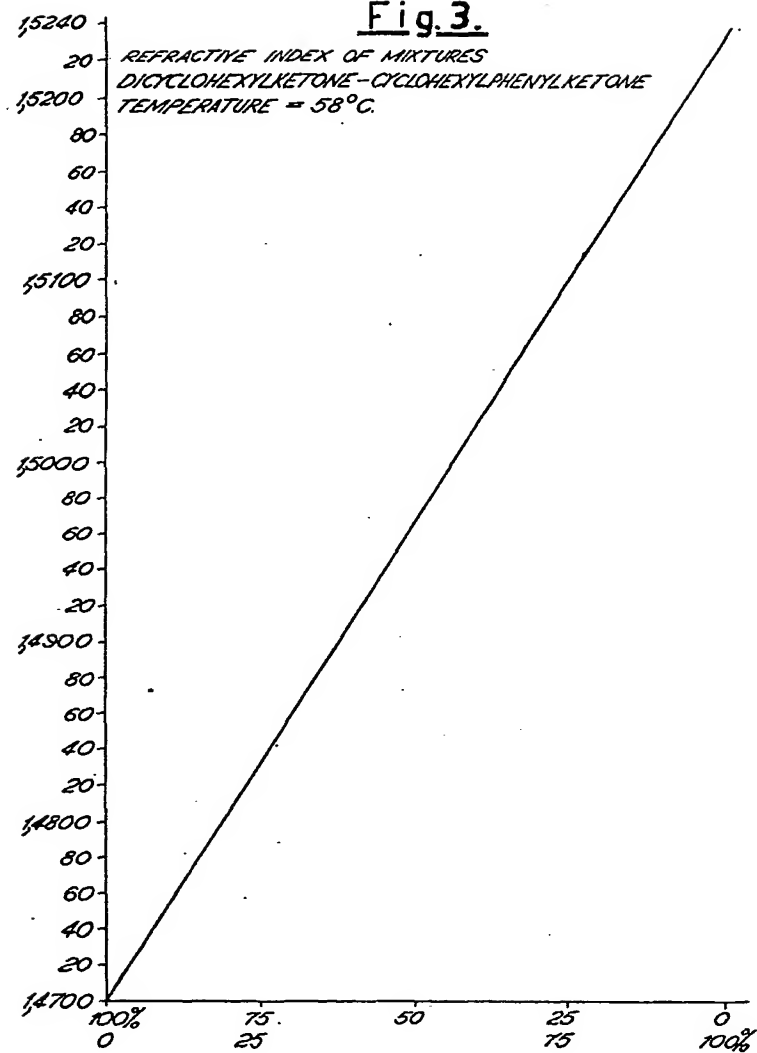


Fig. 3.

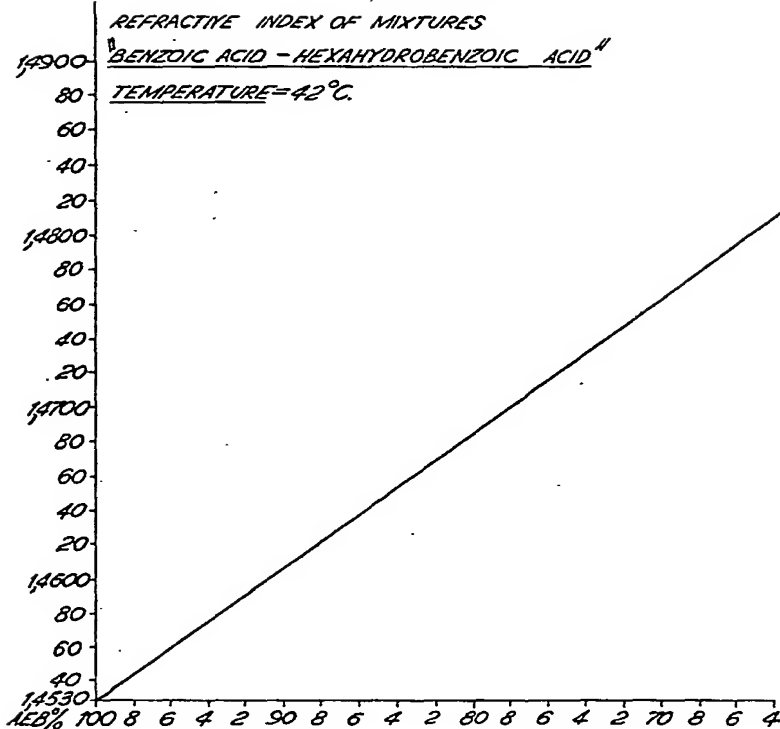


1063268 COMPLETE SPECIFICATION

3 SHEETS This drawing is a reproduction of
the Original on a reduced scale
Sheets 2 & 3

NYLKETONE

Fig.4.



25 0
75 100%